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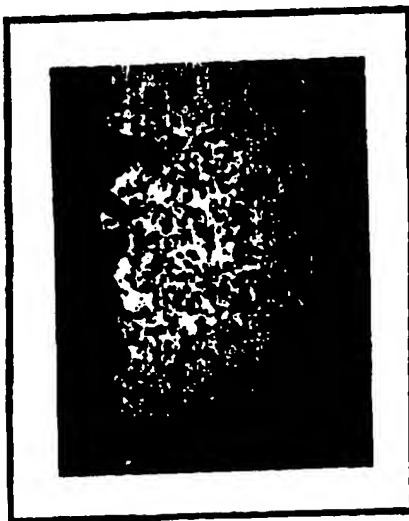
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(54) Title: **MULTI-LAYER PARTICLES FOR ROTATIONAL MOLDING**

Run #1
14 Minutes @ 600°F (10x)
Outside Mold Surface



Run #2
30 Minutes @ 600°F (10x)
Mold Surface

(57) Abstract

Multi-layered, core and shell particles are used to rotationally mold articles. The core and shell materials may be thermoplastic polymers, the difference between the core and the shell will be at least 0.5 melt index units, optionally, the core and shell may also differ by at least about 1 °CT_m. The core and shell particles produce a rotationally molded article with generally an outer layer (of the molded article) that fuses more easily, and an inner layer that may provide superior toughness.

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MULTI-LAYER PARTICLES FOR ROTATIONAL MOLDING

TECHNICAL FIELD

This invention relates generally to improved rotational molded articles.

- 5 More specifically, this invention relates to polymer particles that incorporate a core layer and a shell layer, each layer exhibiting different properties. A rotationally molded part made from such particles will exhibit improved physical properties when compared to a part made with conventional particles. Such particles can facilitate processing conditions more favorable to physical property improvement.

10

BACKGROUND

- Many types of polymers have been used for manufacturing articles by rotational molding where both the polymers and the process are well known in the art, polyolefins are the generally preferred polymer due largely to economics and ease of processing. The rotational molding process utilizes a cavity mold which is suspended on at least one axis, more often on at least two axes. A polymer or polymers to be molded into a hollow part are charged to the mold cavity with a particle size that permits ease of filling all cavities of a mold, as well as rapid melting. The mold is closed and rotation of the mold on at least one axis is begun, concurrent with heating of the mold either from the outside of the mold or from hot gases on the interior of the mold, or both. As the softening point or melting point of the polymer or polymers is reached the polymers begin to fuse or sinter into the shape of the mold cavity. After substantially all of the polymer has fused, the mold still containing the molded article is cooled until the polymer would not be deformed by handling, then the part is removed from the mold. A well executed rotationally molded part will be generally a hollow part or a part having a cavity such as a toy, a surf board, a small boat, a tank or other types of objects with generally uniform properties around the molded part. A more detailed of description of rotomolding can be found in Modern Plastics Encyclopedia, 1985-1986, pg. 319.
- 15
20
25
30

In order to improve rotational object molded physical properties such as impact strength, or environmental stress crack resistance (ESCR), weight average molecular weights (M_w) of the resins are generally increased. However, as with many such relationships, the increase in molecular weight can be beneficial for some physical properties, but detrimental to others causing a trade-off. In this case, a trade-off may be that while increased M_w gives a molded article with improved physical properties, the processability of a higher molecular weight material (M_w) generally becomes more and more difficult with increasing molecular weights, due at least in part to its lower flowability at rotational molding temperatures. The lower flowability is substantially related to the resin's higher viscosity. This problem may be solved in conventional extruder type melt fabrication processes by introducing additional shear and heat to such a polymer via machine changes. However in a rotational molding process there is relatively little shear. Accordingly, creating properly fused or void free parts with increasingly higher molecular weight material becomes problematic because of either economic considerations such as length of time for a molding cycle, or because of dynamics of the process or both. Such process dynamics might include heating the mold to a temperature high enough to fuse the higher molecular weight materials, which might lead to unacceptable degradation, oxidation and/or perhaps charring of the innermost portions of the molded article.

Another factor affecting the ability of a resin or resins to fuse in a rotational mold, substantially free of voids, is the variable heating of a mold. Molds can have hot spots and cold spots due to, for instance, location (near a door, or surrounded by other molds) or heat transfer differences (e.g. where additional heat conductors or insulators inevitably touch the mold).

Attempts have been made in the past to make tougher rotational molded parts, for instance US Patent 5,260,381, discloses a cross-linkable polyethylene based composition for rotational molding. The cross-linking that takes place based on this disclosure delivers a tougher part from a polyethylene resin than would be

attainable by the part in an uncross-linked state. The difficulties with such an approach are that the recycling or reuse of scrap or off-specification products once they are cross-linked is more difficult.

There is a need for a method of producing the rotationally molded parts
5 that are tougher and maybe rotationally molded without use of cross-linking agents.

In US Patent 4,533,696 a method is disclosed for differentially depositing polymer layers in a rotational mold by control of the relative particle sizes of two or more different polymer layers. This approach is known as a salt and pepper
10 blend, referring to a blend of two different components. In the document the two different components are differently stabilized materials to achieve a specific purpose, which is having a well stabilized outer layer for protection of the article from exposure to the elements, while the inner layer is a substantially non-stabilized polymer which is disclosed as oxidizing inside the mold providing a receptive
15 surface for a mold filling such as polyurethane, for example, for use in surf boards.

An article entitled "Processing and Properties of Rotationally Molded Foam", R. L. Heck, Journal of Cellular Plastics, March/April 1993, illustrates the use and typical production of foamed resins via use of various foaming agents. The problems presented with this approach is that different foaming agents must be
20 chosen based on the temperature profile during rotational molding. Often temperatures are different even within a given part causing uneven foamed structure or blistering on the molded part surface.

JP 84-145733 discloses the use of multilayer particles to aid sintering in a non-pressurized environment. However this is accomplished via polymerization in
25 an aqueous process to create latex polymers. This is considerably different from a rotational molding process.

Accordingly, there is a need to have a combination of properties that will permit a rotationally molded article to have relatively easy processing polymer while still exhibiting improved physical properties.

SUMMARY

With embodiments of the present invention, I have found that the above-mentioned disadvantages associated with prior solutions to the problem of obtaining a rotational molding resin that processes relatively easily and has superior toughness, can be solved by the use of particles containing at least two polymers, where at least a first polymer has a different fusing temperature than a second polymer. The second polymer may will impart toughness generally unavailable by conventional rotational molding methods or by use of the first polymer by itself. The first polymer will form a shell substantially covering the second polymer, the second polymer forming a core.

A shell may contain one or more polymers, and a core may contain one or more polymers. The differences discussed below between the melt index (MI) and/or peak melting point (T_m) will still be of importance.

Preferably the shell has a viscosity characterized by melt index, which is at least 0.5 (dg/min) higher than that of the core polymer, at typical test conditions. If the viscosity of the shell polymer is too low (i.e. too a high melt index), the overall binder, which the shell layer becomes, may become too weak and superior part properties may not result. If the viscosity of the shell polymer is too high, poor fusion and voids may result which again generally cause parts with weak physical properties.

Rotationally molded parts made from such a heterogeneous particle, surprisingly show improved physical property performance over salt and pepper particle, pellet, or powder blends.

The heterogeneous particles may be made up of an outer shell of a relatively low melting/fusing polymer where the shell polymer is present in the range of from about 5 to about 70 percent of the total particle diameter. The interior or core of the particle made up of a more difficult to fuse material is present in the range of from about 30 to about 95 percent based on total diameter of the particle. The optimum shell and core distribution is in the range of 70/30 to

30/70. Preferred particles can be as large as about 30 mils (762 microns) in diameter with an aspect ratio defined by the length/diameter ratio of the particle in the range of from about 2:1 to 1:2. The preferred aspect ratio is 1:1. Smaller particles may be made by traditional grinding processes or by extrusion. The preferred diameter is less than about 20 mils (508 microns) and the preferred method of production is extrusion.

The differences between the shell and core polymers may be further enhanced by a difference in peak melting point (T_m) as measured by differential scanning calorimetry (DSC), especially if greater than about 2° C.

Other applications may require different relationships between the shell and core polymers, for instance in a foamed rotationally molded part, the shell polymer may desirably have a higher M_w than the core polymer. Nonetheless, the differences between the shell and core material should still be at least 0.5 dg/min, optionally the T_m should still be at least about 1°C different between the shell polymer or polymers and the core polymer or polymers.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features, aspects, and advantages of embodiments of the present invention will become better understood with regard to the following description, appended claims and accompanying drawings where: Figure 1 shows a photomicrograph at 10X magnification of the molded parts from Runs 1 and 2.

DESCRIPTION

The present invention concerns certain polymer compositions and applications based on these compositions. These polymer compositions have properties when used in a rotational molding which make them particularly well suited for applications that require superior toughness from a rotational molded part. The structure of the particles used to make the rotationally molded articles

deliver a combination of processability and toughness generally superior to previously available materials.

Following is a detailed description of certain preferred polymer compositions within the scope of the present invention, preferred methods of producing these compositions, and preferred applications of these polymer compositions. Those skilled in the art will appreciate that numerous modifications to these preferred embodiments can be made without departing from the scope of this invention. For example, though the properties of the polymer composition are exemplified in rotational molding applications, they will have numerous other uses. To the extent our description is specific, it is solely for the purpose of illustrating preferred embodiments of my invention and should not be taken as limiting the present invention to these specific embodiments. Various values given in the text and claims are determined and defined as follows:

Impact Strength, measured by Association of Rotational Molders (ARM) test using a 15 lb. (6.8 Kg) weight dropped at various heights to give an impact energy in ft - lb._F or Joules. Test done at -40° C.

Part Thickness known as the average part thickness. Measured as mils (1/1000th of an inch), or millimeters using a micrometer.

Cure State can be described as a qualitative measurement of the absence of voids in the part cross-section. Excellent cure has no voids, poor cure has many voids throughout the cross-section.

The Flexural Modulus, at 1% secant, in KPSI (MPa) measured using ASTM D-790.

Instrumented Impact Test (IIT) using a CEAST tester at -40°C. Method follows ASTM D-3763-86.

Environmental Stress Crack Resistance, (ESCR), using ASTM D-1693 Condition A, 10% Igepal solution, on rotationally molded samples 136 mils (3.45 mm) thick. Reading in hours, is taken when 50% of the samples fail (F₅₀).

Viscosity as measured by melt index using ASTM D-1238, Condition E (2160 gm/190° C). Viscosities may also be measured by plate and cone rheometry at 10^{-2} sec⁻¹. Flow units in pascal-sec.

Rotational Molding Cure Time (minutes): Exxon method, using a clam
5 shell rotational molding machine, Model FSP M-60. The time necessary for a rotational molding formulation, typically in granular, micro-pellet, or powder form, to fuse into a void free part at a given temperature. Too little cure time will result in voids or air pockets, too much cure time will degrade the resin from which the part is formed. Resin degradation is exemplified by an increase in resin viscosity
10 (drop in melt index), and/or severe color shifting towards a yellow/brownish part. This may quantified by measuring carbonyl formation on the inside surface of the rotationally molded part, or generally in the industry by using the arm dart impact tests discussed above.

Melt Strength as defined by a method outlined by G. Meissner, Pure &
15 Applied Chemistry, Vol. 42, pg. 553, 1975.

Particle Size Distribution, measured by the amount retained on a screen, as defined by ASTM D-1921 using a Rototap Model B, 100 gm sample, 10 minute shake.

Dry Flow of particles measured in seconds by a Funnel Flow Test, as
20 defined by ASTM D-1895, Method A on a 100 gm sample. High values of dry flow or no flow denote poorer powder quality as the tumbling action of the powder will not be uniform, and this part forming will be poorer.

Bulk Density in g/100 cc as defined by ASTM D-1895, Method A, using a minimum of a 200 gm sample.

Melt Index is defined by ASTM D-1238 using 2160 grams at 190° C, units
25 in gm/10 minutes, or decigrams/minute, dg/min).

Density is defined by ASTM D-1505, units in gm/cc.

Differential Scanning Calorimetry (DSC) by ASTM D-3417.

In an embodiment of the present invention for improved impact strength, a shell and core construction of a particle is comprised of at least one polymer in the shell or outside layer of the particle and at least a second higher molecular weight, (optionally) lower melting point, than the polymer of the shell layer material in the core. The more easily fused polymer (generally the shell polymer) may melt and fill areas in a mold that are intricate or involve sharp angles (whereas a lower MI material would be more difficult to fill in such areas). The shell polymer also as it fuses between the core polymer domains fills in the voids between the particles thus becoming a binder or adhesive layer, creating a substantially void free part. The more difficult to fuse (e.g., lower MI or core) domains trapped and dispersed between and behind (or to the part interior) the binder layer, will have improved impact strength and stress crack resistance so the overall morphology may be similar to conventional rubber modified polymers.

15 Shell Materials

Among the polymers envisioned for the shell are lower viscosity materials such as linear low density polyethylenes with melt indices above about 1.5 dg/min. with densities above about 0.915, preferably above or about 0.930g/cc high density polyethylenes with a melt index above about 1.5 dg/min. and most preferred a density above about 0.940 g/cc; ionomer materials having a melt index greater than about 1.5 dg/min. preferably above about 2.0 dg/min, more preferably above about 3.0 dg/min. and a cation content greater than about 0.5 wt% and; polypropylene having a melt flow MI rate in the range of from about above about 1.0 dg/min. preferably in the range of from about 3 to about 40 dg/min, more preferably from about 5 to about 40 dg/min; ethylene co-polymers of acrylic acid, unsaturated acid or ester comonomers such as acrylic acid, methacrylic acid, methyl acrylate, vinyl acetate, ethyl acrylate, or butyl acrylate having melt indexes greater than about 1.5 dg/min. and comonomer contents greater than about 4 weight percent are generally preferred. More preferred above about 2.0 MI, most preferred above about 2.5.

More preferred comonomer level above about 5 wt%, most preferred above about 8 wt%.

LDPE is also contemplated for the shell material. LDPE's with 1.5 dg/min. are preferred, more preferably greater than about 2 dg/min., and preferred densities greater than 0.915 g/cc, more preferably densities in the range of from about 0.915 to about 0.930 g/cc. LDPE's are generally polymerized in the presence of free radical initiators.

The shell material may be filled with talc, silicas, glass beads, crosslinking agents, or other materials to improve surface abrasion resistance of the finished article. The shell material may also be nylon, SELAR® (DuPont) functionalized PE, fluorinated or sulphonated polymers to improve chemical resistance, again having melt indexes of greater than about 1.5 dg/min. For impact improvements, most preferred for the shell layer will be lower melting point linear low density polyethylenes (LLDPE), high density polyethylenes (HDPE)s, polypropylenes (PP), and ionomers.

For foamed application, the preferred shell material would have a higher viscosity (lower MI) than the core material by at least 0.5 MI units and more preferred by 2.0 MI units. Optionally this could be enhanced by using a higher melt strength material, to aid cell structure formation.

For chemical resistance, the preferred shell material would be a SELAR functionalized PE, or nylon, most preferred a nylon 6.

The LLDPEs, HDPEs, and PP can be made employing metallocene, traditional Ziegler-Natta, and Chromium type catalysts, and catalyst systems. The LLDPE will have a density in the range of from about 0.85 to about 0.940 g/cc preferably in the range of from about 0.90 to about 0.940 g/cc, more preferably from about 0.915 to about 0.940 g/cc. The HDPE will have a density in the range of from about 0.940 to about 0.965 g/cc. The PP will generally have a density about 0.90. The shell materials of an embodiment of the present invention for impact forming improvement will be selected from the group consisting of LLDPE,

HDPE, polypropylene, polypropylene copolymers, ethylene vinyl-acetates, ethylene ethylinically unsaturated acrylic ester copolymers, ionomers, acid co and terpolymers.

5 Core Materials

Core materials for impact improvement are those materials which will be higher molecular weight (M_w), optionally lower melting (than the shell materials), than the materials described for the shell. These will generally be resins that will yield tougher rotationally molded parts. The core materials may be linear low
10 density polyethylene (LLDPE) having a melt index in the range of from about 0.5 to about 10 dg/min., and a density in the range of from about 0.915 to 0.940 g/cc (preferably .915 - .930 g/cc), more preferably the MI will be in the range of from about 0.5 to about 5 dg/min., and most preferably in the range of from about 0.8 to about 4 dg/min.; high density polyethylenes (HDPE) having a melt index in the
15 range of from about 0.05 to about 70 preferably in the range of from about 0.3 to about 5, more preferably in the range of from about 0.3 to about 4.0 dg/min. and densities in the range of from about 0.940 to about 0.960 g/cc polypropylene homopolymers, polypropylene co and terpolymers where ethylene and/or α -olefins having carbon numbers from 4-20 may be used; polyethylenes or polypropylenes,
20 when not homopolymers, can have co and termonomers selected from the group consisting of α -olefins having 4-20 carbon atoms. The comonomer may be selected from the group consisting of butene-1, 4-methyl-1-pentene, pentene-1 hexene-1, octene-1, or any of the alpha-olefins having from 4-20 carbon atoms. In the case of polypropylene, the comonomer may be any of these alpha-olefins but
25 also includes ethylene as potential comonomer. In the case of conventional low density polyethylene (LDPE) comonomers can be selected from ethylinically unsaturated acrylic acid esters. Nylon and other engineering thermoplastics are also contemplated as core materials. The polyethylenes and polypropylenes can be catalyzed by traditional Ziegler-Natta Catalysts, Metallocene/ alumoxane Catalysts,

chromium based catalysts, certain free radical initiated Low Density PE's or LDPE ethylene carbon monoxide copolymers and terpolymers. Preferably the ethylene or propylene co or terpolymer will have a comonomer content in the range of from about 0.5 to 6 mole percent, more preferably in the range of from about 2 to about 6, most preferably in the range of from about 4 to about 6 mole percent. Preferred α -olefins for both ethylene and propylene co and terpolymers are 4-methyl-1-pentene, butene-1, pentene-1, hexene-1, and octene-1.

Also as a core material, nylon is contemplated, having the following properties: melt index greater than about 1.5 dg/min and about densities 1.0 g/cc.

Other preferred core materials will be selected from the group consisting of linear low density polyethylenes, high density polyethylenes, polypropylene, polypropylene copolymers, nylons, and ethylene ethylinically unsaturated ester copolymers or ionomers. LLDPEs, HDPEs, and PPs, and polypropylene and copolymers thereof may be catalyzed by the conventional Ziegler-Natta catalysts, chromium type coordination catalysts, metallocene alumoxane/single site catalysts, or in the case of high pressure polyethylene materials (LDPEs), through free radical initiation polymerization. The ethylene and the propylene polymers may be made by a number of processes including high pressure, gas phase fluidized bed, slurry, or solution processes.

In the selection of core and shell materials a difference in M_w as manifested in MI of at least 0.5 melt index units will achieve the melting and fusing differences of importance. Preferably this difference is at least 1, most preferably 2.5 melt index units. In addition to or in place of the melt index differential, a peak melting point differential (as measured by Differential Scanning Calorimeter (DSC)) of at least about 1° C, preferably at least about 2° C, most preferably at least about 5° C.

For foamed applications the preferred core material would contain a foaming agent. Some foaming agents are azodicarbonamide, p-toluene sulfonyl semicarbazide, p-p-oxobis- (benzene-sulfonyl hydraxide), diphenyloxide-4, 4'-

disulphohydraxide, or p-toluene sulfonylhydrazide. The preferred agent is pp-oxybis (benzene-sulfonyl hydraxide) or diphenyloxide-4, 4'-disulphohydraxide.

The foaming agent can be added at 0.05 wt to 10% wt with a more preferred range of 0.2 to 6 wt % and the most preferred range of 0.3 to 5 wt %

5 The foaming agent can be incorporated by melt extrusion (single screw preferred method), Banbury mixers, 2-roll mills. Melt extrusion via extruders is preferred with single screw extrusion most preferred.

MAKEUP OF CORE AND SHELL PARTICLES

10 A shell is defined and used hereinafter as a material that partially covers and is on the outside of a core material in the range of from about 5 to about 70 percent of the particle diameter, preferably in the range of from about 30-70 percent based on the total diameter of a heterogeneous particle. Preferably the shell material will cover substantially all of the core material. The core material
15 will make up the balance of the particle and will be preferred-substantially covered by the shell material. If the shell material covers less than about 25% of the core material surface area, the same problems that would be encountered with an attempt to rotationally mold the core materials would be encountered, and the benefit the core and shell distribution on a particle may be lost.

20

METHODS OF MAKING A HETEROGENEOUS CORE AND SHELL PARTICLE

25 Methods of forming core and shell polymers include, but are not limited to, coextrusion, powder deposition, or copolymerization. The use of series reactors is a well known way to combine two different polymer properties in the same particle. The size of pellets or particles are typically, 5-100 mils (127-2540 microns) preferred 5-50 mils (127-1270 microns), more preferred 5-30 mils (127-762 microns), most preferred 5-20 mils (127-508 microns) in diameter with and aspect ratio (the ratio of a particle's length to diameter) in the range of from about

2:1 to about 1:2 preferred in the range of from about 1.5:1 to about 1:1.5, most preferred in the range of from about 1:1. The pellets may then be ground to a size typically used in rotational molding, specifically in the range of from about 20 to 2.9 mils (500 to 75 microns) also described as a maximum of 35 US mesh
5 preferred in the range of from about 13.8 to 2.9 mils (350-75 microns), more preferred in the range of from about 11.7 to 2.9 mils (300-75 microns).

Another method of manufacture would be to use a coextrusion technique followed by a strand cutting pelletizing operation or an underwater pelletizing operation. If the pellets or particles are to be used in a rotational molding process
10 they should not exceed about 30 mils (762 microns) preferably, 20 mils (508 microns) most preferably 8 mils (203 microns). Alternatively however, particles of any size may be ground into a powder finer than about 30 mils (762 microns) in diameter, preferably finer than about 20 miles (508 microns).

Whatever method of manufacture is chosen for forming the shell and core
15 materials, whatever the percentage of each particle is, Shell/core, and however complete the encapsulation of the core by the shell, the particle should perform to advantage when compared to for instance salt and pepper blends, or melt blends.

Examples 1-9

20 ID/run numbers 1-9 combine a range of materials in a Killion coextrusion apparatus. Polymer particles are pelletized and then ground in an attrition mill, made by Wedco, USA. The particle distribution is outlined in Table 3. The material from each of the coextrusion tests is run in rotational molding evaluations. These evaluations are carried out in an FSP Model 60 clam shell rotational molding
25 machine, using a sheet mold, cured at 600° F for 14 minutes. The molded polymer is allowed to cool 5 minutes with the top of the oven closed and then 5 minutes with the top of the oven open with ambient air circulated by a fan, followed by 11 minutes of water spray onto the mold and part then a 3 minute period of drying. Where a part was made, the thicknesses are approximately 240 mils (6.1 mm). The

physical properties of the parts molded are shown on Table 4. No physical property testing is done on runs 1-3, as runs 1-3 are only used to illustrate the morphology created. Run 1 illustrates that a 20/80 shell/core polymer structure when ground to a powder, creates a coarse interpenetrating network where the
5 core polymer exhibits domain regions.

Run 2 illustrates that a 50/50 core/shell particle, when ground to 35 mesh particle size provides a continuous network. Comparing Runs 1 and 2, in photos leads us to believe that if a 30/70 structure was created a dense interpenetrating network would be present.

10 Runs 4 and 4B are of most interest relative to improving impact strength. Run 4 utilized a particle according to an embodiment of the present invention, specifically a shell polymer of LL-8460 at 3.3 melt index, 0.939 density, stabilized LLDPE available from Exxon Chemical Canada, with a core material of LL-5005 which is a 0.3 MI, 0.960 density high density polyethylene available from Dow
15 Chemical Canada. Whereas run 4B utilized a more traditional blend, specifically a "salt and pepper" blend of the same two resins of example 4. The parts were cured identically. As can be seen the salt and pepper blend had less than half the impact strength of the heterogeneous particle material at the same thickness. The heterogeneous part also exhibited a better cured state. Additionally, the
20 heterogeneous particle molded article displayed well over 100% increase in ESCR when compared to the salt and pepper blend.

Runs 6-9 show other combinations though none were optimized and none were satisfactory.

25 Example 10

To create a rotationally molded part having relative impermeability to solvents a SELAR (R) material is used in the shell. The "platelets" formed by the SELAR provide a difficult or torturous path for a Solvent to traverse. Additionally a high crystallinity polymer such as nylon is also employed to provide relative

impermeability to solvent penetration. When SELAR® is used as the shell material and LLDPE is used as a core material, a part having excellent solvent barrier, but good impact strength at reduced cost is produced.

5 Example 11

 A dense interpenetrating network, especially containing conductive fillers, is used in the shell to improve static charge dissipation. Relatively high MI materials e.g. 5 MI LLDPE (density 0.930 g/cc) containing aluminum flakes, carbon black and conductive fibers are used in the shell to provide a combination of
10 inter-penetrating network with conductive fillers to more easily facilitate dissipation of static build. The core material used a LLDPE with a 0.5 MI lower than the shell material. The core material provides enhanced impact strength. Compared to the filled polymer used by themselves in a rotationally molded part, the parts made from the core and shell does play superior impact resistance.

15

 Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. For example, other means of forming heterogeneous particles, and other combinations of polymers are contemplated. Therefore, the spirit and scope of the
20 appended claims should not be limited to the description of the preferred versions contained herein.

TABLE I
MULTI-LAYER POLYMER SAMPLE DESCRIPTION

I.D.	<u>Description</u>		<u>Details</u>	<u>End Use Idea</u>
	<u>Shell Polymer</u>	<u>Core Polymer</u>		
1	DUEX 1637	LL-8460	• 20% ⁽²⁾ Strand Diameter Shell ⁽¹⁾ , 80% Core	• None - to study distribution in final part.
2	DUEX 1637	LL-8460	Total diameter 5 mm (205 mil) • 50% Shell, 50% Core, 5mm diameter total	• None - to study distribution in final part.
3	DUEX 1637	LL-8460	• 80% Shell, 20% Core, 5mm diameter total	• None - to study distribution in final part.
4	LL-8460	LL-5005	• 80% Shell, 20% Core, 5mm diameter total	• Tougher molded part.
6	HX-350	PP-7032	• 80% Shell, 20% Core	• Stiffer molded part.
7	HX-350	EXACT 4042	• 80% Shell, 20% Core	• Tougher.
8	LL-8460	Rilsan RDG-133T	• 20% Shell, 80% Core	• Fuel resistance.
9	Iotek 8030	LL-8460	• 20% Shell, 80% Core Start	• Tougher

(1) Should have - 184 mil core with outer shell width around 21 mil.

(2) 20% means 20% of total cross-section diameter is this polymer.

TABLE 2
DETAILED DESCRIPTIONS OF RAW MATERIALS FOR MULTI-LAYER POWDER

<u>Grade</u>	<u>Form</u>	<u>Description</u>
• LL-8460.27	Pellets	• LLDPE, 3.3 MI, .939 D, Well Stabilized. Supplied by Exxon Chemical Canada
• DUEX 1637	Pellets	• 12 MI, .928 D, LLDPE Black Masterbatch. Supplied by Wedtech, Inc.
• PP-7032	Pellets	• Homopolymer Polypropylene - 4MFR, .90D. Supplied by Exxon Chemical Americas.
• HX-350	Pellets	• HDPE, 5 MI, .948 D, Good Stabilization. Supplied by Exxon Chemical Canada.
• Iotek 8030	Pellets	• Sodium Ionomer. Supplied by Exxon International, Inc.
		2.8 MI, .955 D, EAA Based, (2-3% Active AA Left)
• Nylon 11 - Rilsan RDG-133T	Powder	• Good Stabilization - Not Highly Hydrophillio. Supplied by A. Schulman, Inc.
• EXACT 4042	Pellets	• 1.2 MI, 90D Polyethylene, Stabilized Sufficiently for Extrusion. Supplied by Exxon Chemical Americas.
• LL-5005	Pellets	• 0.3 MI, .960 D Blowmolding Grade of HDPE. Supplied by Dow Chemical Canada.

TABLE 3
GRINDING DATA

US Mesh Size, % Retained on (2).

Run	35	50	60	80	100	120	Pan	Dry Flow, (Seconds(1))
4(a)	0.7	34.7	24.2	22.5	5.9	5.8	6.2	No flow
4(b)	0.2	41.4	23.5	19.7	4.8	4.5	4.9	No flow
1	0.8	35.2	21.8	21.5	6.1	6.7	7.6	No flow
3	0.9	49.6	72.6	17.0	3.8	3.2	2.9	19.7
8	0.5	27.5	22.2	26.4	7.5	8.2	7.7	No Flow
2	2.2	49.4	16.6	17.1	3.9	4.6	6.1	No Flow
6	0.4	32.8	29.9	25.3	5.0	6.5	5.4	—
7	0.3	32.8	23.4	24.9	4.7	7.1	6.6	No Flow
8	0.1	28.7	20.7	25.5	4.7	9.3	11.0	38.11
9	1.1	33.9	27.5	30.3	1.8	3.3	2.1	No Flow

(1) Dry flow is a measure of powder tumbling or flow quality. The lower the number generally the better. No flow is a very high value and thus poorer quality. Test details outlined in ASTM D 1895.

(2) Particle size analysis, ASTM D-1921. Look for most of material to be in 50-80 mesh levels if ground powder for rotational molding.

TABLE 4
MULTI-LAYER POLYMER WORK - PHYSICALS
 (WR 93TSD-116)

Run Number Description	1 CB(2) Some Fusion	2 CB Poor Fusion	3 CB Poor Fusion	4 Multi-layer BM Resin With LL-8460 14 min. @ 600° F	4B Ribbon Blended BM Resin With LL-8460 14 min. @ 600° F	6 HX-350 and PP 14 min. @ 600° F	7 HX-350 and E-4042 14 min. @ 600° F	8 Nylon & LL- 8460 14 min. @ 600° F	9 Iotek and LL- 8460
FSP(1)									
RM Conditions (Hex Mold)									
ARM Impacts									
• -40° C, 15 lb. tup	-	-	-	111	59	5	15	101	-
• Thickness, mil	-	-	-	230	240	240	240	240	-
• Cure State	-	-	-	Better Cure	Undercured	Undercured	Excellent	Excellent	-
Flexural Modulus,	-	-	-	75.5	-	108	94.0	75.0	84
1% Secant, (Kpsi)									9.0
IIT Impacts, CEAST, -40° C									
Energy Total (Joules)									
ESCR, F(50) Hours,									
10% Igepal									
RM Samples	-	-	-	168	70	-	-	-	240
136 mil Thick									

(1) 5 minutes oven cool, 6 minutes rotation lid open, 11 minutes water spray, 3 minutes dry off.

(2) CB Means carbon black

CLAIMS**I Claim:**

- 5 1. A method of producing shaped articles by;
including in a rotational mold, polymer particles, characterized in that said
polymer particles have a core and a shell, wherein
- 10 a) said core includes a polymer selected from the group consisting
of HDPE, LLDPE, LDPE, PP, polypropylene copolymer, ionomer,
and nylon, preferably HDPE and LLDPE, more preferably LLDPE;
- 15 b) said shell includes a polymer selected from the group consisting
of HDPE, LLDPE, LDPE, ethylene copolymers of ethylenically
unsaturated carboxylic acid esters, and ionomers, preferably HDPE
and LLDPE, more preferably LLDPE;
- 20 wherein said core and shell polymers differ by at least 0.5 melt index units,
preferably by at least 1 melt index unit, more preferably at least 2.5 melt
index units;
- 25 wherein said core is at least partially encapsulated by said shell, preferably
said shell polymer is present in said polymer particle in the range of from 5
to 70 percent, preferably 30 to 70 percent based on the total diameter of
the polymer particle;
- wherein said polymer particle size does not exceed 1016 microns,
preferably 889 microns; and
- 30 wherein said core and said shell polymers differ by at least 2°C in T_m ,
preferably 5°C.

2. In rotational molding process, a molded article being formed by:
charging polymer particles to a mold, heating and rotating said mold;
- 5 characterized in that said polymer particles are multilayered particles
wherein at least a first polymer is substantially encapsulated by a second
polymer;
- 10 wherein said first and said second polymer differ in melt index by at least
0.5 dg/min, preferably at least 1 dg/min, more preferably at least 2.5
dg/min;
- 15 wherein said polymer particles have a size between 127 and 1270 microns,
preferably 127 to 762 microns, most preferably 127 to 508 microns; and
wherein said polymer particles have an aspect ratio in the range of from 2:1
to 1:2, preferably 1.5:1 to 1:1.5, more preferably 1:1.
3. The process of claim 2 wherein said multilayered polymer particles are
ground to a size between 75 to 500 microns, preferably 75 to 350 microns.
- 20 4. The process of claim 2 wherein said first polymer is selected from the group
consisting of LLDPE, LDPE, HDPE, PP and ionomers;
- 25 wherein said second polymer is selected from the group consisting of
LLDPE, HDPE, and polypropylene; and
- 30 wherein said first and second polymers differ in melt index by at least 1,
preferably 2.5 melt index units, and
- wherein said first and second polymers differ in T_m by at least 1°C,
preferably 2°C, more preferably 5°C.

5. The process of claim 2 wherein said first and said second polymers are the same or different, preferably wherein both said first and said second polymers are LLDPE.

5

6. The process or method of claims 1 or 2 wherein said core or first polymer contains a foaming agent;

10 said foaming agent being selected from the group consisting of p-toluene sulfonyl semicarbazide, p-p-oxobis- (benzene-sulfonyl hydraxide), diphenyloxide-4, 4'-disulphohydraxide, or p-toluene sulfonylhydrazide;

wherein said foaming agent is present in the range of 0.2 to 6 weight percent, preferably in the range of 0.3 to 5 weight percent.

15

7. The process or method of claims 1 or 2 wherein said shell or second polymer partially covers said core or first polymer in the range of 5 to 70 percent, preferably 30 to 70 percent, based on the total diameter of the polymer particle.

20 8. In a process for forming rotationally molded articles, characterized in that said articles are formed by:

25 placing a plurality of core and shell polymer particles in a mold, rotating said mold in at least one axis, and heating said mold containing said particles;

30 wherein said core and said shell polymers are selected from the group consisting of LLDPE, HDPE, LDPE and ionomer, wherein said core and shell polymers are the same or different, preferably where both said core and shell polymers are LLDPE;

wherein said shell polymer covers said core polymer in the range of 30 to 70 percent, based on the total diameter of the polymer particle;

5 wherein said core and shell polymer differ in melt index by at least 2.5 dg/min;

wherein said core and shell polymers differ in T_m by at least 5°C;

10 wherein said core and shell polymer particle have a size in the range of 127 to 508 microns; and

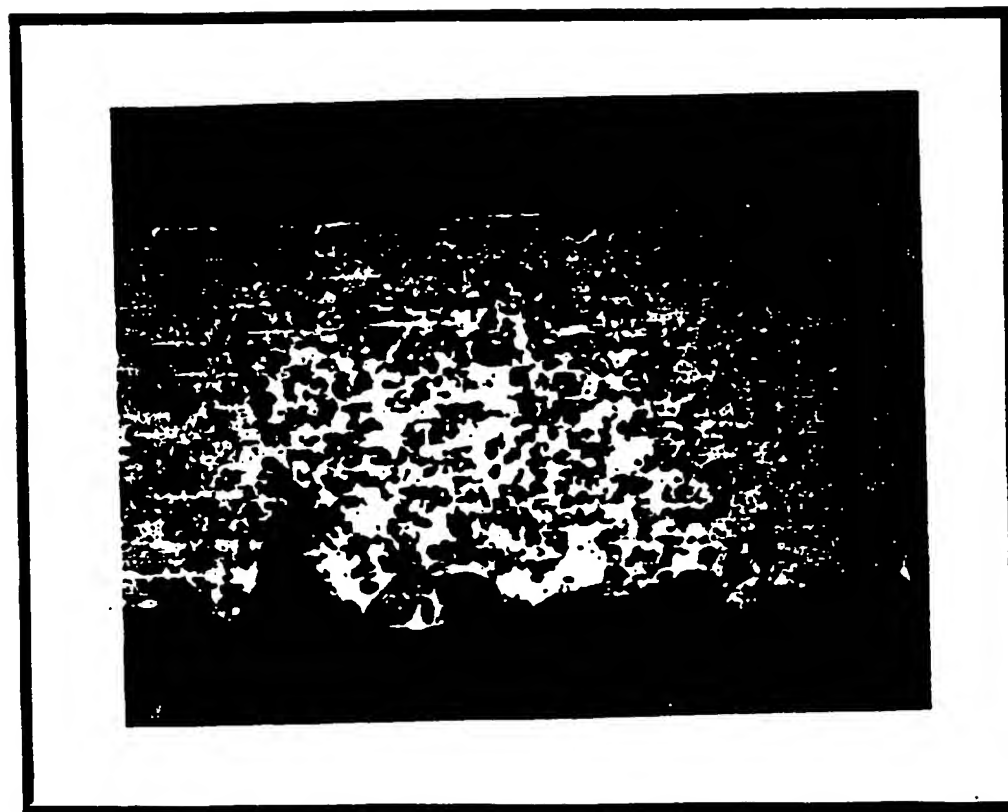
wherein said particles have an aspect ratio of 1:1.

15 9. The process of claim 8 wherein said core and shell polymer particles are ground to a size in the range of from 75 to 300 microns.

10. The process or method of claims 1, 2, or 8 wherein said shell or second polymer contains a filler selected from the group consisting of talc, silica, glass
20 beads, cross linking agents and combinations thereof.

11. Use of the processes of claims 2 or 8, or the method of claim 1, to make a toy, a surfboard, a small boat, or a tank.

FIGURE 1



Run #1
14 Minutes @ 600°F (10x)
Outside Mold Surface



Run #2
30 Minutes @ 600°F (10x)
Mold Surface

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/14401

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29B9/12 B29C41/04 C08J3/12 C08J9/224 //B29K23:00,
B29K77:00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B29B C08J B29C C09J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X A	WO,A,95 19877 (THE QUEEN'S UNIVERSITY OF BELFAST) 27 July 1995 see the whole document ---	1,2,4,5 6
P,Y A	US,A,5 366 675 (DONALD G. NEEDHAM) 22 November 1994 see the whole document ---	1,8-11 6
X Y	DE,A,39 06 478 (EMS-INVENTA) 13 September 1990 see the whole document ---	2-5 1,8-11
A	DE,A,42 37 637 (BASF AG) 11 May 1994 see the whole document ---	1-5,8
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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* "A" document member of the same patent family

Date of the actual completion of the international search

12 April 1996

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/US 95/14401

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	<p>EP,A,0 209 294 (DU PONT CANADA) 21 January 1987 see the whole document see page 7, line 20</p> <p>-----</p>	1,2,4,8

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Information on patent family members

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PCT/US 95/14401

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EP-A-209294	21-01-87	JP-A- 62079244	11-04-87